1,3,2-BIPHENYLDIOXABOREPIN (2,2'-BIPHENOXYBORANE) AS A NEW HYDROBORATING AGENT.
DIRECTIVE EFFECTS IN THE HYDROBORATION OF THE ALKENES AND ALKYNES

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Abstract - 2,2'-Biphenoxyborane (1,3,2-biphenyldioxaborepin, 1), readily avail-
able from the reaction of 2,2'-biphenol with borane in THF, reacts with alkenes
readily at $25^{\circ}C$, or rapidly at $68^{\circ}C$, and with alkynes rapidly at $25^{\circ}C$, to give
the corresponding alkyl- and alkenylbiphenoxyboranes in high yields. These hy-
droboration reactions proceed stereospecifically in a cis manner. A similar re-
gioselectivity to catecholborane is realized with a greater reactivity.

As one of the newly developed hydroboration reagents, partially substituted boranes,[2] catecholborane[3]
appears to be an interesting and useful one for both alkenes[4] and alkynes[5] upon heating to provide,
for the first time, a convenient synthesis of alkane- and alkeneboronic esters and acids. These hy-
droborations proceed stereospecifically and regioselectively.[4-6] However, the reaction of alkenes
and alkynes at normal temperature, such as at room temperature, is very slow. The reaction requires
elevated temperatures for sufficient hydroboration rate ($100^{\circ}C$ for alkenes and $70^{\circ}C$ for alkynes).[3]
In the course of developing new hydroborating agents, we observed that borane reacts rapidly at $-10^{\circ}C$
with 2,2'-biphenol in THF to form 1,3,2-biphenyldioxaborepin (2,2'-biphenoxyborane, 1) (eq.1).[7]

$$\text{(1)}$$
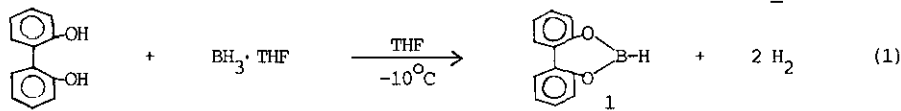
This disubstituted borane reacts readily with alkenes at 25 or $68^{\circ}C$ and rapidly with alkynes at $25^{\circ}C$
to give the corresponding alkyl- and alkenylbiphenoxyborane in high yields (eq.2). The products un-

$$\text{(2)}$$
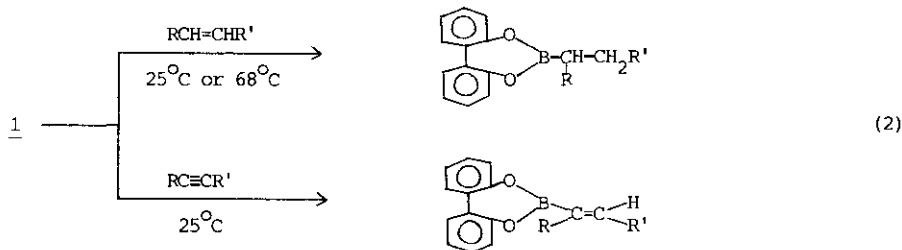
dergo hydrolysis rapidly to give the corresponding alkane- and alkeneboronic acids.
The reagent is stable at least for 6 months at $0^{\circ}C$ when kept under dry nitrogen. The B-11 nmr spec-
trum of 1 in THF showed a broad doublet centered at δ 9.4 ppm (J_{B-H} = 121 Hz). The reagent without
further purification is good enough for hydroboration reactions.
The rate of hydroboration of various alkenes with 10 mole% excess 1 in THF is summarized in Table 1.
The hydroboration of terminal alkenes at room temperature was usually completed within 24 or 48 h.
Heating to the reflux temperature (ca. $69^{\circ}C$) accelerated the hydroboration reactions to be complete

Table 1. The Rate of Hydroboration of Alkenes with 2,2'-Biphenoxyborane in Tetrahydrofuran at Room Temperature[a]

Alkenes	Time, h	Hydride used for hydroboration[b]
1—decene	1.0	0.53
	6.0	0.65
	12.0	0.78
	24.0	0.91
	48.0	1.00
	0.5[c]	0.71
	1.0	0.84
	2.0	0.93
	4.0	1.00
	1.0[d]	1.00
1-octene	1.0	0.58
	6.0	0.77
	12.0	0.95
	24.0	1.00
	1.0[d]	1.00
1-pentene	1.0	0.62
	6.0	0.80
	12.0	0.96
	24.0	1.03
	1.0[d]	1.01
3,3-dimethyl-1-butene	1.0	0.65
	6.0	0.82
	12.0	0.90
	24.0	1.00
	1.0[d]	1.00
2,3-dimethyl-2-butene	1.0	0.42
	6.0	0.66
	12.0	0.75
	24.0	0.87
	48.0	0.92
	72.0	1.00
	1.0[d]	0.84
	3.0[d]	1.01
2,4,4-trimethyl-2-pentene	1.0	0.23
	6.0	0.35
	12.0	0.44
	24.0	0.61
	48.0	0.73
	72.0	0.82
	120.0	0.99
	1.0[d]	0.62
	3.0[d]	0.83
	6.0[d]	1.00
cyclohexene	1.0	0.39
	6.0	0.50
	12.0	0.58
	24.0	0.65
	48.0	0.80
	72.0	1.00
	1.0[d]	0.89
	3.0[d]	1.01
1-methylcyclohexene	1.0	0.37
	6.0	0.43
	12.0	0.49
	24.0	0.64
	48.0	0.80
	72.0	0.98
	96.0	1.00
	1.0[d]	0.74

	3.0[d]	0.92
	6.0[d]	1.01
styrene	1.0	0.53
	6.0	0.65
	12.0	0.79
	24.0	0.90
	48.0	1.00
	1.0[d]	1.00
α-methylstyrene	1.0	0.43
	6.0	0.56
	12.0	0.68
	24.0	0.75
	72.0[d]	0.98
	1.0[d]	0.89
	3.0[d]	1.01

a) 10 Mol % excess reagent used : 0.5 M in compound. b) Mmoles of reagent per mole of compound. c) At 50°C. d) Under reflux.

within 1 h. The rate of hydroboration of hindered internal alkenes, such as 2,3-dimethyl-2-butene and 2,4,4-trimethyl-2-pentene, was much slower, requiring 3 and 5 days for completion respectively, but under reflux the reaction was completed within 6 h. Cyclohexenes examined also underwent hydroboration readily. It required 3 or 4 days for complete hydroboration at room temperature. This reagent also readily hydroborated styrene, however the methyl substitution on the double bond retarded the rate of hydroboration, requiring 3 days at room temperature. The reaction was accelerated upon heating to be complete within 3 h. In general, the rate of hydroboration with biphenoxyborane appears to be much faster than that with catecholborane.[3,4]

The directive effects in the hydroboration of alkenes with 1 were also investigated. After standard hydroboration with the reagent (10% excess) under reflux, the product in each case was oxidized with alkaline hydrogen peroxide, and the oxygenated products were identified by gc analysis. The results are summarized in Table 2.

Table 2. Directive Effects in the Hydroboration of Alkenes with 2,2'-Biphenoxyborane under Reflux[a]

Alkenes	Time, h	Total yield of 3 (%)	% composition	
			α product[b]	β product[b]
1-decene	1	96	97	3
	4[d]	95	98	2
	48[e]	97	98	2
1-octene	1	96	97	3
1-pentene	24[e]	92	97	3
3,3-dimethyl-1-butene	1	94	98	2
1-methylcyclohexene	6	94	99.5	0.5
2,4,4-trimethyl-2-pentene	6	95	10	90
styrene	1	96	91	9
α-methylstyrene	3	96	99	1

a) 10 Mol % excess reagent used. b) By gc analysis of the oxygenated products after oxidation with alkaline hydrogen peroxide. c) Position of the attachment of boron in $R-C_\beta=CH_\alpha$ or $R-CH_\beta-CH_\alpha-CH_3$. d) At 50°C. e) At 25°C.

The reagent shows a high selectivity in placing the boron atom preferentially at the less hindered carbon atom, in similar to that of catecholborane.[3] Especially, in the hydroboration of alkylated 1-alkenes, such as 1-methylcyclohexene and α-methylstyrene, the selectivity reaches essentially 100%.

The monohydroboration of alkynes with this reagent in the stoichiometric ratio (1:1) was performed in THF at room temperature and the results are summarized in Table 3.

Table 3. The Rate of Monohydroboration of Alkynes with 2,2'-Biphenoxyborane in Tetrahydrofuran at
Room Temperature[a]

Alkynes	Time, h	Hydride used for hydroboration[a]
1-heptyne	0.5[b]	0.63
	3.0[b]	0.79
	6.0[b]	0.92
	12.0[b]	0.93
	24.0[b]	0.94
	0.5	0.83
	1.0	0.90
	3.0	1.00
1-hexyne	0.5	0.90
	1.0	0.95
	3.0	1.00
2-hexyne	0.5	0.83
	1.0	0.89
	3.0	1.00
3-hexyne	0.5	0.75
	1.0	0.84
	3.0	0.92
	6.0	1.00
3,3-dimethyl-1-butyne	0.5	0.95
	1.0	1.00
phenylethyne	0.5	0.82
	1.0	0.95
	3.0	1.00
1-phenylpropyne	0.5	0.75
	1.0	0.77
	3.0	0.85
	6.0	0.90
	12.0	0.99
diphenylacetylene	0.5	0.69
	1.0	0.70
	3.0	0.77
	6.0	0.80
	12.0	0.92
	24.0	1.00

a) An equivalent of reagent used : 0.5 M in each compound and reagent in THF. b) At 0°C.

The rate data in Table 3 reveal that, in general, terminal alkynes undergo slowly hydroboration at
0°C, but at room temperature the reactions are rapidly completed within 3 h for terminal alkynes
and 6-24 h for internal alkynes. Again, the reactivity of this reagent toward alkynes appears to be
much higher than that of catecholborane, which requires the reaction temperature of 70°C for ob-
taining a satisfactory rate.[3,5]
The directive effects in the monohydroboration of terminal alkynes and unsymmetrically substituted
internal alkynes were also examined and the results are summarized in Table 4.

Table 4. The Directive Effects in the Monohydroboration of Alkynes with 2,2'-Biphenoxyborane at
Room Temperature

Alkynes	Time, h	Total yield of **3** (%)	% composition	
			α product[b]	β product[b]
1-hexyne	3	92[c]	94	6
1-heptyne	3	93[c]	94	6
3,3-dimethyl-1-butyne	1	95[c]	99	1

phenylethyne	3	96[a]	90	10
3-chloropropyne	3	91[c]	81	19
2-hexyne	3	90[a]	61	39[d]
diphenylethyne	24	96[a]	(50)[d]	(50)[d]
1-phenylpropyne	12	96[a]	84	16

a) The reaction product was oxidized, and the oxygenated products were determined by gc analysis.
b) Position of the attachment of boron in $R-C_\beta=CH_\alpha$ or $R-C_\beta=C_\alpha-CH_3$. c) By gc analysis of the mono-hydroboration product. d) Theoretical ratio.

As is evident from the data, both the steric and electronic natures of the substituents play major roles in affecting the direction of addition of the B-H bond. 1-Hexyne and 1-heptyne gave 94% of the terminal hydroboration products, the corresponding aldehydes. 3,3-Dimethyl-1-butyne, with the greater steric requirement, afforded exclusively the terminal hydroboration product, 99%. Phenyl-ethyne and 3-chloropropyne showed the considerable electronic effects of these substituents. Phe-nylethyne, for example, gave a mixture of the isomeric carbonyl compounds, produced by the alkaline hydrogen peroxide oxidation of the reaction mixture, in 96% yield, of which only 90% was phenyl-acetaldehyde with the remaining 10% of acetophenone coming from attack of this reagent at the in-ternal position, in a similar pattern of catecholborane.[3]

In the monohydroboration of unsymmetrically disubstituted alkynes with the reagent, the results re-veal that the boron atom attacks preferentially on the carbon atom at the less hindered position of the triple bond. The electronic effect of the phenyl substituent also comes to be considerable, but the steric influence is still dominant in placing the boron atom on the less hindered carbon atom. In addition, the nmr spectral examination of alkeneboronic esters obtained by the hydrobora-tion of 1-alkynes with 2,2'-biphenoxyborane revealed that the addition of the boron-hydrogen bond to the triple bond occurs in a stereospecific cis manner.

The reagent, 2,2'-biphenoxyborane (1,3,2-biphenyldioxaborepin, 1), was prepared as follows. A 1.2 M solution of borane in THF[2d] (250 ml, 300 mmol), maintained under nitrogen, was placed in a dry 1-l flask which was connected to a hood vent through a mercury bubbler. The flask was cooled to -10°C using an ice-salt bath, and a pre-cooled solution of 2,2'-biphenol (57.56 g, 309 mmol) in THF (200 ml) was added over 1 h to the borane solution with stirring at -10°C. After completion of the addi-tion, the reaction mixture was stirred for an additional 2 h at that temperature. The reagent was found to be at least 95% pure according to B-11 nmr spectral analysis. This reagent (0.65 M) in THF was directly used for further reactions.

The following procedure for the reaction of 1-decene is representative for determination of the rates and the directive effects of hydroboration of alkenes and alkynes. A 100-ml flask, equipped with a side arm and a condenser connecting to a mercury bubbler, was charged with 16.9 ml of the borepin 1 solution (11 mmol), 1.40 g of 1-decene (10 mmol) and a sufficient amount of THF (1.2 ml, the reaction mixture to be 0.5 M in the olefin). The reaction mixture was then heated to be under reflux, while the whole system was maintained under nitrogen. Hydrolyzing of aliquots with a mix-ture of glycerin-water-methanol (1:1:1) at appropriate intervals revealed the hydroboration to be essentially complete in 1 h.

Into a flask containing 8 ml of the reaction mixture, 0.68 g of dodecane (4.0 mmol) as a standard was injected and the mixture was cooled at 0°C. The oxidation was done by the dropwise addition of 3 N sodium hydroxide (6.7 ml, 20 mmol) followed by the dropwise addition of 30% hydrogen peroxide (2.7 ml, 8 mmol) at 0°C. The temperature was subsequently brought to room temperature. The mixture was then stirred for 2 h, diluted with water, and extracted with pentane after saturation with po-tassium carbonate. The extract was washed with brine, dried with anhydrous magnesium sulfate, and subjected to gc analysis : 97% yield, comprising 1-decanol (97%) and 2-decanol (3%). The oxidation

of 2-alkenyl-1,3,2-biphenyldioxaborepin with hydrogen peroxide and sodium hydroxide was similarly carried out.

It is evident that development of 2,2'-biphenoxyborane as a selective and reactive monofunctional hydroboration reagent for alkenes and alkynes should find wide application, especially in cases where milder reaction conditions than those catecholborane requires[3-5] be essential. The hydroborations of catecholborane proceed practically at 100°C for alkenes and 70°C for alkynes, whereas 2,2'-biphenoxyborane undergoes hydroboration practically at room temperature or under reflux for alkenes and at room temperature for alkynes. We are also currently investigating the reducing characteristics of this reagent, which will appear in a journal shortly.

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7. Alternatively, 2,2'-biphenoxyborane can be prepared by the reaction of 2,2'-biphenol and borane-dimethyl sulfide (BMS) in the presence of excess boron trifluofide etherate.